

SWIFT & COMPANY
RESEARCH & DEVELOPMENT CENTER
PACKERS & EXCHANGE AVENUES
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INTERIM REPORT FOR 12 MONTHS
ENDING JULY 31, 1967
CONTRACT NAS 7-487

PROJECT LEADER

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INTRODUCTION

In general, the objectives outlined in our original proposal to Jet Propulsion Laboratory have been attained. The outline presented under the heading of "Plan of Approach", has been carried out and a film has been developed having the best possible combination of properties comprising all the variables studied. During the course of the work, Mr. D. D. Lawson of Jet Propulsion Laboratory requested that our work include consideration of the behavior of gelatin when tested with a torsion pendulum. The emphasis was on the properties of gelatin after it had been subjected to cryogenic temperature ranges. It was recognized that a complete study could only be done by extending the span of this contract. For this reason this report is only an interim final report and the contract has been extended from twelve to twenty-four months.

OUTLINE

The objectives to be attained in this effort for the first twelve months were:

1. Provide protein films of various thicknesses derived from:
 - a. Swift's Superclear gelatin.
 - b. Deaminated gelatin.
 - c. Carbamidated gelatin.
 - d. Cyanamidated gelatin.
 - e. Phenol-formaldehyde resin-gelatin condensate.
2. The use of plasticizers in these films at various levels:
 - a. None.
 - b. Ethylene glycol.
 - c. Polyethylene glycol.
 - d. Dimethylsulfoxide.
 - e. N-Methylpyrrolidone.
 - f. Glycerol.
3. The use of crosslinking agents at various levels:
 - a. Formaldehyde.
 - b. Glyoxal.

3. (Cont'd),
 - c. Glutaraldehyde.
 - d. Other.
4. The use of reenforcing fibers:
 - a. Glass fibers.
 - b. Cattle hair.
 - c. Collagen.
 - d. Cellulose fibers.
5. Statistical analysis of the data.
6. Special case of glycerol:
 - a. Optimum level.
 - b. Three gelatin types tested.
 - c. Final selection.
7. Special treatments of films.
 - a. None.
 - b. Ultra-violet irradiation.
 - c. Heat treatment.
 - d. Cryogenic temperature treatment.
8. Comprehensive evaluation for gas impermeability using:
 - a. Hydrogen.
 - b. Helium.
 - c. Oxygen.
 - d. Nitrogen
 - e. Carbon dioxide.
9. Tensile strength determinations in pounds per square inch.

10. Torsion pendulum

- a. Preparation of massive specimens..
- b. Equipment.

11. Future work.

12. Financial.

PREPARATION OF FILMS

Swift's Superclear Gelatin

The basic product for this work was Swift's Superclear Gelatin, a gelatin of 300 gram test with a natural pH of 3.9-4.1. It was extracted from acid cured pork skins for maximum jelly strength and minimum viscosity. The grind used was 6-20 a designation which signified the mesh range. Such a product was free of fines and did not hydrate excessively fast and permitted the production of almost any concentration of gelatin with minimum entrapment of air.

DEAMINATED GELATIN

Deaminated gelatin was prepared by the reaction with nitrous acid on the amino groups with the formation of hydroxy groups. Three different levels of deamination were carried out in order to select the one most suited for film preparation. For the purpose of calculations, gelatin was considered to contain 46 milliequivalents of amino groups per 100 grams of gelatin. On this basis, three lots of deaminated gelatin were prepared using the theoretical, 0.5 the theoretical and 0.1 the theoretical amount of sodium nitrite.

These samples on drying were found to be incompletely soluble and thus had to be rejected. The factors responsible for the lack of complete solubility were narrowed down to: amount of nitrous acid, temperature of deamination and insolubilization resulting from complete drying.

The preparation of a satisfactory lot of deaminated gelatin was accomplished as follows:

Four hundred fifty grams of gelatin were soaked in 2500 ml. of distilled water for several hours. The gel was then melted on a water bath at 39-40°C. Nine grams of sodium nitrite dissolved in 100 ml. of water were added dropwise with mechanical stirring over a ten minute period. The reaction mixture was allowed to stand for twenty minutes and poured into trays to chill. The gelatin sheets were cut into strips, dialyzed in running tap water at 15-17°C for 24 hours. The swelled strips were partially dried in the air and then cut into 0.5 inch cubes. These were held in a cooler for 48 hours to equilibrate the moisture content and then assayed for gelatin content. The gelatin content was 17.53% gelatin. The moist cubes were packaged in 250 gram lots in Mylar bags and frozen in a sharp freezer until needed.

CARBAMIDATED GELATIN

The preparation of carbamided gelatin was carried out by reacting gelatin with potassium cyanate. Under the conditions of the experiment the cyanic acid reacted with the amino groups to yield substituted ureas. The same problem of partial insolubility was encountered if the carbamided gelatin was dried completely, therefore, the following procedure was developed and used to produce a soluble carbamided gelatin.

Four hundred fifty grams of Swift's Superclear gelatin were soaked in 2500 gms. of distilled water. After melting at 40°C., nine grams of potassium cyanate dissolved in 100 ml. of water were added with stirring and allowed to react for 25 minutes. The mixture was poured into trays, chilled, cut into 1/2" wide strips and dialyzed for 24 hours in 15-17°C water. The dialyzed product was partially dried in an air tunnel, cut into small pieces and packed in Mylar bags and frozen. The solids content was 20.7%.

CYANAMIDATED GELATIN

Cyanamided gelatin was made just before the solution was cast into a film. This had to be done because of the very limited life of gelatin solutions after the addition of hydrogen cyanamide. The level of hydrogen cyanamide used was at the rate of 42 milliequivalents of hydrogen cyanamide for 100 gms of gelatin. The material was conveniently measured out with a micro pipette as a 50% aqueous solution.

PHENOL-FORMALDEHYDE CONDENSATE-GELATIN

Phenol-formaldehyde condensate solutions were prepared and added to the gelatin just before pouring onto the film plates. A number of preparations of a water soluble phenol-formaldehyde resin based on the procedure of d'Allelio, (Experimental Plastics and Synthetic Resins, John Wiley & Sons, (1960), p. 16) were prepared. None of these were found to be water soluble in all proportions. A product made according to the following directions was found to be suitable and homogeneous after having added to it 5% of ethanol.

PREPARATION OF A SOLUBLE PHENOL-FORMALDEHYDE CONDENSATE

A mixture of 376 grams of crystalline phenol and 420 grams of formalin catalyzed with 3.2 gms. of sodium hydroxide dissolved in 20 ml. of water were heated in a flask on a glycerol bath at 120 + 5°C with stirring under reflux for 45 minutes. Cooled at once in an ice bath and neutralized with 0.1 M citric acid and concentrated at 30°C in a "Rinco" evaporator under vacuum. After several days no further material was being removed and the residue was cut with water. The heterogeneous solution was rendered homogeneous by the addition of 5% alcohol. The resin content was 22.2%.

PLASTICIZERS

The plasticizers originally considered were: glycerol, ethylene glycol, polyethylene glycol, propylene glycol, dimethylsulfoxide, N-methyl pyrrolidone. These were made up as aqueous solutions and were colored for easy identification.

CASTING SURFACES

The casting surfaces were clean plate glass one foot by two feet. An area 55 x 15 cm. was outlined with a chinamarker pencil to enclose an area of 825 cm². Using a density of 1.33 for gelatin, we find that 2.8 gms. of gelatin spread out over this area yielded a film one mil (.001 inch) thick.

Summarizing, the basic formula became:

2.8 grams of gelatin

28 mgs. of dried ox bile (1% basis gelatin)*

x% plasticizer basis the gelatin
added as a 2.8% aqueous solution.

Add sufficient water to permit the 825 cm² to be covered. The total water ranged from 80 to 100 ml. depending upon the amount of dissolved solids.

*The ox bile acted as a release agent without which gelatin films could not be removed from glass surfaces.

Thicker films were made by multiplying the basic formula by the film thickness desired. The initial set of films was limited to gelatin alone, a total of 180 different films being produced. Of the 180 films prepared we have examined many to evaluate their gas permeability in a general way. The calibration and testing of our equipment using these early films indicated the following:

1. Helium consistantly diffused through the films at about twice the rate of hydrogen, thereby permitting us to speed up the screening of films using helium.

2. Our gas permeability determination when run on four replications of 4 mil gelatin films plasticized with 5% glycerol yielded the following results. Results are as cc/100 in²/24 hrs./atm.

2.2 cc repeating on the same sample - 2.1 cc

2.5 cc " " " " " - 2.3 cc

2.0 cc " " " " " - 2.2 cc

2.3 cc " " " " " - 2.2 cc

A statistical evaluation of the magnitude of the significant limits yielded a difference of 0.2cc/100 sq.in./24 hrs./atm. This is to say that differences of 0.2 cc or greater are significant in 95% of the cases. However, this is true only of these films, having this thickness, composition and formulation. Other films will no doubt have other differences.

In a preliminary way the following premeabilities to gases were measured in cc/100 in²/24 hrs./atmos.

2 mil Gelatin Film

2% Glycerol Plasticizer He = 5.0, A = .034, O₂ = 0.1

5% " " He = 4.8, A = 0.3, O₂ = 0.02

5 mil Gelatin Film

5% Glycerol He = 1.9, 2.2; O₂ = 0.006

5 mil Gelatin Film

3% Ethylene Glycol He = 2.9; O₂ = 0.02

5% " " He = 2.5; H₂ = 1.8; O₂ = 0.01

These permeabilities were re-run on the films prepared as part of a statistically designed series.

Pursuant to Mr. Lawson's request for an approximate cohesive energy density calculation we have obtained a value using the equation $\delta^2 = (\Delta H_v - RT)/v$ as reported in the Encyclopedia of Polymer Science and Technology, Volume 3, page 834. Predicated on water being the only solvent for gelatin we have $\Delta H_v = 539.5 \times 18.02$ cal/mol; $RT = 1.387 \times 373.16$ and $V = 22.4$ liters. Therefore, $\delta^2 = 400$ approx. and $\delta = 20$. approx.

It became evident that the number of specimens would have to be reduced because of the limitations of the contract. Also, the supply of gelatin proved to be inadequate. Therefore, a new supply of gelatin sufficient for the contract was obtained. Our Division of Statistics and Experimental Design recommended a design for the production of 165 films from 5 varieties of gelatin, with 5 plasticizers at 3 levels and 3 thicknesses of film. The design was coded as follows:

Plasticizers

- 1 - Ethylene glycol (green)
- 2 - Polyethylene glycol (red)
- 3 - Dimethyl sulfoxide (yellow)
- 4 - N-Methylpyrrolidone (purple)
- 5 - Glycerol (no color)

Gelatin

- 1 - Gelatin
- 2 - Deaminated gelatin
- 3 - Carbamidated gelatin
- 4 - Cyanamidated gelatin
- 5 - Phenol-formaldehyde condensate and gelatin.

Thickness

- 1 - 1 mil.
- 3 - 3 mil.
- 5 - 5 mil.

Levels

- 0 - 0%
- 1 - 2%
- 2 - 5%

The above variables indicated 225 trials but these were reduced of 165 because one of the levels of plasticizers was zero and one determination at this level could be used for all plasticizers. The samples were randomized so as to yield additional information about the experimental error.

FILM PREPARATION

The preferred method of casting a film was as follows: The required amount of gelatin or frozen gel in the case of deaminated or carbamidated gelatin was combined with 1% dry ox bile, the required amount of aqueous plasticizer and enough water to total 80 cc of water for 1 mil films, 90 ml of water for 3 mil films and 100 ml of water for 5 mil films. The mixture was melted in 130-140°F water bath and held long enough to be free of bubbles before pouring. The cyanamidated and phenol-formaldehyde resin treated samples had the required amount of additive added at this point and were poured on glass. Samples which could be expected to release poorly were poured on Mylar film cemented to glass plates. Generally, these were the cyanamidated and phenol-formaldehyde resin-gelatin preparations.

Generally, the best films were obtained when the drying took place at a leisurely rate. In the case of relative humidity extremes, difficulties were encountered. Drying and release were poor in the case of high relative humidity. At low humidity, static attraction was so great that the films on snapping off the support would be strained and often would shatter because they were attracted so strongly that they could not adjust to the changing forces in the film. The films were stored flat in envelopes until required for testing. Samples of film were conditioned at 73°F and 50% relative humidity for at least 18 hours before being tested for helium transmission and tensile strength.

Gas transmissions were determined in accordance with ASTM Method D 1434-58 using a Dow Gas Transmission Cell manufactured by Custom Scientific Instruments, Inc.

Gas transmission rate in method is determined from measurements of the pressure and volume change of gas transmitted through the specimen from a chamber of gas at a specified temperature and at a static and essentially constant pressure and into an initially evacuated, calibrated manometer. The gas transmission rate is the steady state volume of test gas, converted to standard temperature and pressure which passes through a known area of specimen per unit of time. Steady State is defined as that state of test conditions at which the volume of test gas transmitted becomes linear with time.

The Gas Transmission Cell was operated using the adapter designated by manufacturer for the determination of slow or low range transmission rates. The gas used was Grade A Helium manufactured by the Dept. of Interior, Bureau of Mines. The average pressure difference between opposite sides of the cell was 750 mm mercury and the manometer deflection was observed through a 50 mm mercury change. The test area of the specimen is 10./sq. cm. The tests being conducted at 73°F and 50% RH.

The rate being reported in cubic centimeters per square inch per 24 hours corrected to standard temperature and pressure.

The Tensile Breaking Strengths were determined in accordance with ASTM Method D 828-60 using a Schaffer Tensile Apparatus manufactured by Testing Machine Inc., of New York.

The test specimens were cut to 1 inch width and the test conducted with a 2" initial gap between the jaws at a speed of 1 foot per minute. The tests being conducted at 73°F and 50% RH.

A portion of the evaluation was complicated by a change in the character of the films themselves arising from a change in the environment. All of these films were prepared by casting onto a glass surface and permitting the film to dry at ambient temperature and humidity. As the fall season advanced, the relative humidity in the laboratory underwent a continuous change to lower values. The rate of film drying was speeded up correspondingly resulting in uneven drying. This in turn produced strains in the film at the point where the dry film joined the wet film resulting in the formation of ridges or waves on the film surface. These ridges then made the formation of a gas tight seal in the gas transmission cell quite impossible. About thirty-one specimens were repeated and dried in the test room at 50% relative humidity. The majority of these replicates formed satisfactory films under these conditions and those that did not were repeated and dried in a cooler at 35°F. All but two yielded usable films.

Steady
measured volume change and pressure which passes
through a known area of specimen per unit of time. Steady
state of test conditions at which the volume
transmitted becomes linear with time.

The complete set of results is given below using symbols to prevent cluttering of the table. The code used for the different variables is given below:

Plasticizers

- 1 - Ethylene glycol.
- 2 - Polyethylene glycol.
- 3 - Dimethyl sulfoxide.
- 4 - N-Methylpyrrolidone.
- 5 - Glycerol.

Gelatins

- 1 - Swift's Superclear gelatin.
- 2 - Deaminated gelatin.
- 3 - Carbamidated gelatin.
- 4 - Cyanamidated gelatin
- 5 - Phenol-formaldehyde condensate and gelatin.

Thicknesses

- 1 - 1 mil.
- 3 - 3 mil.
- 5 - 5 mil.

Levels

- 0 - 0% basis gelatin.
- 1 - 2% " "
- 2 - 5% " "

<u>GELATIN</u>	<u>PLASTICIZER</u>	<u>LEVEL</u>	<u>THICKNESS</u>	<u>HELIUM TRANSMISSION cc/100 in.2/ 24 hrs./atm.</u>	<u>TENSILE STRENGTH POUNDS PER SQ. INCH.</u>
1	1	0	1	13.06	7845
2	1	0	1	27.87	3410
3	1	0	1	16.1	7490
4	1	0	1	13.4	6630
5	1	0	1	8.8	7920
1	1	1	1	13.81	6185
2	1	1	1	17.2	6870
3	1	1	1	15.9	6960
4	1	1	1	15.9	6660
5	1	1	1	11.7	6720

<u>GELATIN</u>	<u>PLASTICIZER</u>	<u>LEVEL</u>	<u>THICKNESS</u>	<u>HELIUM TRANSMISSION CC/100 in.²/ 24 hrs./atm.</u>	<u>TENSILE STRENGTH POUNDS PER SQ. INCH.</u>
1	2	1	1	20.92	7040
2	2	1	1	26.09	7960
3	2	1	1	8.5	10410
4	2	1	1	22.3	6150
5	2	1	1	15.42	5400
1	3	1	1	15.1	4560
2	3	1	1	16.9	5870
3	3	1	1	16.75	6750
4	3	1	1	12.6	5370
5	3	1	1	1.98	7220
1	4	1	1	12.6	4340
2	4	1	1	15.57	6490
3	4	1	1	26.17	2975
4	4	1	1	11.96	6500
5	4	1	1	15.0	7080
1	5	1	1	14.88	6270
2	5	1	1	15.04	6390
3	5	1	1	16.31	9940
4	5	1	1	10.9	5490
5	5	1	1	12.7	5400
1	1	2	1	21.18	7000
2	1	2	1	31.3	6000
3	1	2	1	16.38	5780
4	1	2	1	11.7	6640
5	1	2	1	13.4	6330
1	2	2	1	not available	
2	2	2	1	18.58	7220

<u>GELATIN</u>	<u>PLASTICIZER</u>	<u>LEVEL</u>	<u>THICKNESS</u>	HELIUM TRANSMISSION cc/100 in. ² / 24 hrs./atm.	TENSILE STRENGTH POUNDS PER SQ. INCH.
3	2	2	1	18.6	6950
4	2	2	1	13.4	6370
5	2	2	1	19.82	6530
1	3	2	1	9.3	6700
2	3	2	1	24	5650
3	3	2	1	34.4	5260
4	3	2	1	14.2	6780
5	3	2	1	13	8020
1	4	2	1	13.2	8200
2	4	2	1	25.75	6820
3	4	2	1	20.94	7190
4	4	2	1	15.42	6580
5	4	2	1	13.3	6630
1	5	2	1	10.1	4880
2	5	2	1	20.9	6140
3	5	2	1	15.1	4130
4	5	2	1	9.9	8330
5	5	2	1	6.7	3540
1	1	0	3	4.6	13130
2	1	0	3	13.2	6850
3	1	0	3	3.14	12330
4	1	0	3	5.51	11490
5	1	0	3	5.2	11900
1	1	1	3	4.2	7800
2	1	1	3	8.1	13890
3	1	1	3	7.4	9080

<u>GELATIN</u>	<u>PLASTICIZER</u>	<u>LEVEL</u>	<u>THICKNESS</u>	HELIUM TRANSMISSION cc/100 in. ² / 24 hrs./atm.	TENSILE STRENGTH POUNDS PER SQ. INCH.
4	1	1	3	3.64	11850
5	1	1	3	12.1	10340
1	2	1	3	4.41	11670
2	2	1	3	6.08	13030
3	2	1	3	4.71	14830
4	2	1	3	10.46	12380
5	2	1	3	5.13	11430
1	3	1	3	15.1	6040
2	3	1	3	11.41	6450
3	3	1	3	5.39	12370
4	3	1	3	36.6	14450 Pinholes suspected
5	3	1	3	3.11	11590
1	4	1	3	9.9	8330
2	4	1	3	5.7	12140
3	4	1	3	6.32	12100
4	4	1	3	2.4	11550
5	4	1	3	3.3	9340
1	5	1	3	2.68	11930
2	5	1	3	7.5	9800
3	5	1	3	3.5	12340
4	5	1	3	3.94	12000
5	5	1	3	2.64	17420
1	1	2	3	3.3	9821
2	1	2	3	6.6	9700
3	1	2	3	6.65	10460
4	1	2	3	4.96	11680

<u>GELATIN</u>	<u>PLASTICIZER</u>	<u>LEVEL</u>	<u>THICKNESS</u>	HELIUM TRANSMISSION cc/100 in. ² / 24 hrs./atm.	TENSILE STRENGTH POUNDS PER SQ. INCH.
5	1	2	3	9.4	10290
1	2	2	3	7.69	11450
2	2	2	3	5.7	13370
3	2	2	3	8.8	12950
4	2	2	3	4.92	12890
5	2	2	3	5.02	13490
1	3	2	3	4.5	6470
2	3	2	3	7.85	7110
3	3	2	3	4.3	12630
4	3	2	3	5.23	8370
5	3	2	3	not available	
1	4	2	3	3.3	12100
2	4	2	3	10.1	7230
3	4	2	3	73.7	12600 Flyer- N.G.
4	4	2	3	4.3	11580
5	4	2	3	4.71	11460
1	5	2	3	3.94	11740
2	5	2	3	2.34	6410
3	5	2	3	4.54	11870
4	5	2	3	3.05	7680
5	5	2	3	2.54	10880
1	1	0	5	2.73	16610
2	1	0	5	4.23	12930
3	1	0	5	4.28	14640
4	1	0	5	3.8	8780
5	1	0	5	2.44	15600

<u>GELATIN</u>	<u>PLASTICIZER</u>	<u>LEVEL</u>	<u>THICKNESS</u>	HELIUM TRANSMISSION cc/100 in. ² / 24 hrs./atm.	TENSILE STRENGTH POUNDS PER SQ. INCH.
1	1	1	5	2.58	12800
2	1	1	5	5.4	12620
3	1	1	5	7.91	7590
4	1	1	5	2.3	13950
5	1	1	5	2.1	10200
1	2	1	5	2.26	14710
2	2	1	5	4.78	13030
3	2	1	5	not available	
4	2	1	5	8.17	16380
5	2	1	5	7.1	11770
1	3	1	5	2.59	14960
2	3	1	5	3.38	12050
3	3	1	5	3.7	13320
4	3	1	5	3.3	11700
5	3	1	5	3.14	8230
1	4	1	5	2.9	12030
2	4	1	5	2.86	14090
3	4	1	5	3.85	15070
4	4	1	5	2.51	11410
5	4	1	5	2.64	16550
1	5	1	5	3.16	9730
2	5	1	5	3.8	10720
3	5	1	5	3.81	8390
4	5	1	5	2.23	11530
5	5	1	5	1.82	15420

<u>GELATIN</u>	<u>PLASTICIZER</u>	<u>LEVEL</u>	<u>THICKNESS</u>	<u>HELIUM TRANSMISSION cc/100 in.²/ 24 hrs./atm.</u>	<u>TENSILE STRENGTH POUNDS PER SQ. INCH.</u>
1	1	2	5	1.8	11450
2	1	2	5	2.79	15420
3	1	2	5	4.28	12620
4	1	2	5	1.97	16180
5	1	2	5	2.46	8500
1	2	2	5	3.38	11610
2	2	2	5	3.1	14460
3	2	2	5	2.8	9350
4	2	2	5	3.8	10890
5	2	2	5	3.1	12590
1	3	2	5	4.59	9170
2	3	2	5	3.68	11530
3	3	2	5	3.22	12110
4	3	2	5	2.7	9600
5	3	2	5	3.17	9990
1	4	2	5	3.3	12670
2	4	2	5	9.8	14700
3	4	2	5	2.8	15000
4	4	2	5	4.2	5670
5	4	2	5	2.5	11020
1	5	2	5	1.6	14260
2	5	2	5	5.81	8980
3	5	2	5	3.3	9400
4	5	2	5	3.73	6110
5	5	2	5	2.7	11250

The analysis of the data supplied by our Experimental Statistics Division is made part of this report and is attached below:

One hundred fifty points were taken from the data available to get estimations of effects of gelatins, plasticizers, levels of plasticizers and film thicknesses on gas transmission. The points analyzed did not take into account the zero level of plasticizers.

Analysis of variance showed most main effects as significant and no interactions (only 2 way interactions were examined) as significant.

The mean gas transmission values are given for the main effects which were significant.

I. Film Thickness

<u>Thickness</u>	<u>Average</u>
1 mil.	16.07 cc.
3 mil.	5.89 cc.
5 mil.	3.70 cc.

The mean values all differ significantly from each other. Taking 1 mil and 16.07 cc's as a base value, and assuming transmission is inversely related to thickness, the expected values for 3 mil would be 5.36 (as opposed to 5.89) and for 5 mil 3.21 (as opposed to 3.70). The data thus substantiates the inverse relationship fairly well.

II. Plasticizers

<u>Type</u>	<u>Average</u>
1. Ethylene glycol	8.95 cc
2. Polyethylene glycol	9.46 cc
3. Dimethyl sulfoxide	8.74 cc
4. N-Methyl pyrrolidone	8.84 cc
5. Glycerol	6.79 cc
6. Control (Zero Level)*	8.56 cc

*15 observation for mean rather than 45 as with 1, 2, 3, 4, 5.

The basic difference is that plasticizer glycerol results in significantly lower gas transmission. All other plasticizers did not significantly differ from one another.

III. Gelatin

1. Gelatin	7.64
2. Deaminated gelatin	11.02
3. Carbamidated gelatin	9.74
4. Cyanamidated gelatin	7.43
5. Phenol formaldehyde condensate and gelatin	6.95

At 95% confidence, the following differences are significant. #2 and 3 are significantly higher than #1, 4 and 5. There are no differences between 1, 4 or 5.

IV.

Level of plasticity did not significantly affect gas transmission. Mean for 2% was 8.491, mean for 5% was 8.621. Plasticizer at 0 level has mean 8.560.

In summary, the lower gas transmissions are associated with thick films, glycerol and either gelatin alone, cyanamidated gelatin or phenol-formaldehyde condensate and gelatin. The differences stated as significant are based on an error term estimated by the higher interaction. There were also four missing values which were estimated by a row x column mean value. Thus the analysis given here serves as an estimation only, and modification will no doubt be necessary.

The significantly lower gas transmission value for films containing glycerol when compared with the control without glycerol suggested that the presence of glycerol improves the resistance of the film to helium transmission. The fact that the 5% level of glycerol was better than the 2% level indicated only that the higher level was better but provided no information as to the optimum level. The determination of this optimum level of glycerol will be taken up later. The similarity of the values found for the other four plasticizers when compared with zero level suggested that they are inert as far as influencing the gas transmission. This was further evidence that glycerol had a special place as a gelatin plasticizer.

On the basis of the information contained in the statistical analysis, the following selections were made:

A. In the area of the type of gelatin:

1. Swift's Superclear Gelatin.
2. Cyanamidated gelatin.
3. Phenol-formaldehyde condensate and gelatin.

B. In the area of plasticizers:

1. Glycerol - 5%
2. None

C. In the area of film thickness:

1. Nominally one mil

Summarized this means that we had six variations to be evaluated with the selected crosslinking agents.

CROSSLINKING AGENTS

The need for a suitable method for introducing known amounts of crosslinking agents into a film restricted us to the addition of known amounts of the crosslinking agent in liquid or solid form. For example, treatment of films with gaseous formaldehyde would have been too inexact because there would have been no adequate control over the actual amount of crosslinking agent picked up by the film.

The initial object of this search for a way to crosslink our films was to determine the amounts of crosslinking agent that could be added to a formulated gelatin solution without causing it to gel and at the same time form a dry film that would be hot water insoluble. It was assumed that the minimum amount of crosslinking required to do this would also bring about a significant change in the gas transmission of the film.

In order to prevent premature gelation, all crosslinking agents were added as 1.0% solutions. The basic gelatin formulation used was:

14 gms Swift's Superclear Gelatin

140 mgs. ox bile.

25 ml. of 2.8% Glycerol.

75 ml. water

The chosen amount of formaldehyde was added to each melted sample, mixed and cast onto a glass plate. After drying the films were judged by their behavior in hot water. The results so obtained are summerized in the table below:

<u>No.</u>	<u>ml. of 1.0% Formaldehyde</u>	<u>% Formaldehyde basis Gelatin</u>	<u>Behavior in Hot Water</u>
1.	1.4 ml	0.1	dissolved
2.	4.2 ml	0.3	soluble but less readily
3.	5.6 ml	0.4	insoluble
4.	7.0 ml	0.5	insoluble
5.	10.0 ml	0.75	insoluble

The above results were obtained with concentrations of gelatin used to produce films nominally five mils thick. Formulation number four was chosen as being most applicable to all film thicknesses.

GLYOXAL AS A CROSSLINKING AGENT

Glyoxal levels and concentrations were chosen in a similar manner as shown in the table below:

<u>No.</u>	<u>ml. of 1% Glyoxal</u>	<u>% Glyoxal basis Gelatin</u>	<u>Solubility in hot water</u>	<u>Film at 72°C for 1 hr.- Sol. in hot water</u>
1.	1.4	0.1	soluble	
2.	5.0	0.36	soluble	
3.	10.0	0.72	soluble	insoluble
4.	15.0	1.07	soluble	insoluble

The less reactive nature of the glyoxal could be explained by its pronounced tendency to hydrate and to form acetals with the hydrated forms. Since this reaction is reversed by heat, the crosslinking after one hour at 72°C brought about the required water insolubility. The level of glyoxal selected was the 0.72% level basis gelatin.

GLUTARALDEHYDE

The optimum level of glutaraldehyde was chosen from the following series:

<u>No.</u>	<u>ml. of 1% Glutaraldehyde</u>	<u>% Glutaraldehyde basis Gelatin</u>	<u>Solubility in hot water</u>
1	1.4	0.1	Soluble
2	5.0	0.36	Partially soluble
3	7.5	0.54	Insoluble
4	10.0	0.71	Insoluble
5	15.0	1.07	Insoluble

Allowing for some margin of safety we elected to use the 0.7% level basis gelatin.

OTHER CROSSLINKING AGENTS

The use of hexamethylene tetramine was tried because of the slow rate with which it reacts with proteins. However, none of its reaction products with gelatin were insoluble and because it offered no advantages, no further effort was made to use it.

The initial set of eighteen crosslinked unsupported gelatin films had to be repeated because the films could not be removed from the plate glass without destruction. A second set of films was cast onto Mylar films laminated to plate glass using a pressure sensitive adhesive. The material used was obtained from the Universal Coating Company, 2320 E. 26th Street, Minneapolis 6, Minn.

The range of conditions of these eighteen films included three types of gelatin, namely, Swift's Superclear gelatin, carbamidated gelatin and phenol formaldehyde condensate-gelatin. The glycerol plasticizer was held at two levels, namely, 0% and 5% basis gelatin. Finally, all samples were crosslinked with one of three crosslinking agents; formaldehyde, glyoxal and glutaraldehyde.

The experimental conditions for preparing these films were so similar that the procedure for a gelatin film plasticized with 5% glycerol and crosslinked with formaldehyde could serve as a model for all of them.

2.8 Grams of Swift's Superclear gelatin, 28 mg. of powdered ox bile, 80 ml. of distilled water and 5 ml. of 2.8% aqueous glycerol were mixed and allowed to swell for one hour. The swelled gelatin was melted at 50°C in a water bath while covered with a watch glass. After melting, complete mixing by careful stirring was apparent by the absence of schlieren. Immediately prior to casting the film, 1.4 ml of 1% aqueous formaldehyde was added and gently stirred in. The resulting clear, bubble free solution was poured onto the casting surface and allowed to dry spontaneously without any artificial air movement. Twenty four hours later the film was peeled off, conditioned at least eighteen hours at 73°F and 50% relative humidity and evaluated for helium transmission and tensile strength.

The following table summerizes the compositions and the test results:

NO.	GELATIN GRAMS	OX BILE mg.	WATER	ml. of 2.8% GLYCEROL	ml. of 50% HYDROGEN CYANAMIDE	ml. of 32.8% PHENOL FORMAL-DEHYDE CONDENSATE	ml. of 1% FORMAL-DEHYDE	ml. of 1% GLYOXAL	ml. of 1% GLUTARALDEHYDE	HELIUM TRANSMISSION cc/100in ² /24 hrs/atm.	TENSILE STRENGTH lbs/in ² .
1	2.8	.28	80	5			1.4			10.07	5100
2	2.8	.28	85	-			1.4			21.54	4560
3	2.8	.28	80	5	0.2		1.4			11.08	4570
4	2.8	.28	85	-	0.2		1.4			Holes	5695
5	2.8	.28	80	5		.06	1.4			11.3	4360
6	2.8	.28	85	-		.06	1.4			12.97	5530
7	2.8	.28	80	5				2		9.46	4930
8	2.8	.28	85	-				2		12.51	4540
9	2.8	.28	80	5	0.2			2		10.89	4300
10	2.8	.28	85	-	0.2			2		35.2	5200
11	2.8	.28	80	5		.06		2		9.5	4095
12	2.8	.28	85	-		.06		2		Holes	6010
13	2.8	.28	80	5					2	10.7	3710
14	2.8	.28	85	-					2	24.9	2296
15	2.8	.28	80	5	0.2				2	13.8	3670
16	2.8	.28	85	-	0.2				2	19.17	5180
17	2.8	.28	80	5		.06			2	13.82	3630
18	2.8	.28	80	-		.06			2	22.16	5820

The analysis of data revealed that crosslinking had no significant effect on the helium transmission. However, the level of glycerol had a very strong positive effect on the impermeability of the film to helium. The tensile strength was much less effected by the various changes in the film formulations.

OPTIMUM GLYCEROL LEVEL

The indisputably lower helium transmission of the 5% glycerol samples suggested that there might be a still more effective level of glycerol. In order to find out if this was indeed so, the following screening test was performed:

No.	GELATIN GMS.	OX BILE mg.	% GLYCEROL BASIS GELATIN	WATER cc	He TRANS- MISSION	TENSILE STRENGTH
1	2.8	28	5	90	15.84	7620
2	2.8	28	8	87	17.06	5720
3	2.8	28	11	84	13.3	4090
4	2.8	28	14	81	9.84	5560
5	2.8	28	17	78	8.05	6230
6	2.8	28	20	75	28.8*	4990
7	2.8	28	23	72	11.4	5950
8	2.8	28	26	69	9.8	5510
9	2.8	28	29	66	10.07	4780

*

- Suspected outlier

The results of the screening test suggested that the most useful glycerol content probably lay between 8 and 18% glycerol basis the gelatin. The following series was set up in order to determine this value for each type of gelatin.

SWIFT'S SUPERCLEAR GELATIN

<u>% GLYCEROL</u>	<u>GELATIN GMS.</u>	<u>OX BILE mg.</u>	<u>2.8% GLYCEROL cc</u>	<u>WATER ml.</u>	<u>HELIUM TRANS- MISSION cc/100in.²/ 24 hrs/atm.</u>	<u>TENSILE STRENGTH lbs/in.²</u>
8	2.8	28	8	90	17.73	4340
10	2.8	28	10	90	15.51	5950
12	2.8	28	12	90	14.25	4330
14	2.8	28	14	90	13.85	4400
16	2.8	28	16	90	11.46	6780
18	2.8	28	18	90	12.12	4020

CYANAMIDATED GELATIN

8	2.8	28	8	90	15.28	6020
10	2.8	28	10	90	13.12	5020
12	2.8	28	12	90	17.73	5560
14	2.8	28	14	90	12.32	4660
16	2.8	28	16	90	16.15	4860
18	2.8	28	18	90	21.54	5520

PHENOL FORMALDEHYDE CONDENSATE - GELATIN

8	2.8	28	8	90	brittle	
10	2.8	28	10	90	"	
12	2.8	28	12	90	11.75	5550
14	2.8	28	14	90	19.50	5800
16	2.8	28	16	90	10.80	4280
18	2.8	28	18	90	15.4	4750

Inspection of the data indicated that there were no substantial differences between gelatins and that unmodified gelatin yielded the most consistent results. In the handling of these films, it was noticed that the films made from modified gelatins tended to break more easily and tended to invite damage more rapidly. For these reasons we have decided to restrict further experimentation to Swift's Superclear gelatin alone with a plasticizer content of 16 percent.

REENFORCING FIBERS

a. Glass Fibers.

The use of chopped glass fibers as reenforcing agents for gelatin films was abandoned because it was found impossible to mat the individual fibers into the film. The probable explanation is that the solvent had no effect on the fibers and consequently these were too stiff to form a mat.

b. Cattle Hair.

The use of cattle hair appeared to be impractical because films made with it behaved as if they were full of pin holes. Presumably, the gas is able to travel along or through the hair shaft and thus pass through the film. In addition, the relatively large size of the fibers when compared to the film thickness made it unlikely that a satisfactory combination could be found.

c. Collagen.

The use of reconstituted collagen from dry collagen fibers failed to yield lump free films. In connection with other work we have made films using ratios of gelatin to collagen comprising 2 to 1, 1 to 1 and 1 to 2 using fresh collagen fibers.

The method of preparing films from this form of collagen was as follows: The gelatin was made up as a 2 1/2% aqueous solution after swelling and melting at 45°C. After cooling to 30-35°C, the pH was adjusted to 2.6 with lactic acid. The gelatin solution was then blended with the required amount hydrated collagen dispersed in the necessary amount of water. The blending was done in a Hobart dough mixer and forced through a filter screen. Deaeration was effected in a vacuum chamber without gelation difficulties. The mass was cast into non-orientated films on Mylar coated plates and allowed to dry in a stream of unheated air. Films of this type exhibited tensile strengths of 12000 + 2000 psi which was comparable to gelatin alone, however nothing was known of their behavior regarding gas transmission or elastic properties at cryogenic temperatures. In order to develop such information we proposed to make films by the above described method limiting ourselves to a ratio of two parts of gelatin to one part of collagen. The excessively high

viscosity of the mixture caused us to revise the proportions of collagen to gelatin to a one to one ratio.

Gelatin-Collagen Ratio, 1 to 1.

150 gms of frozen collagen and 850 of distilled water were slurried in a Hobart mixer at 21°C. 41.5 gms of gelatin (containing 37.5 gm of anhydrous gelatin) were swelled and dissolved in 1500 gms of distilled water. After melting and cooling to 35°C, the pH was adjusted to 3 with 85% lactic acid (app. 7 gms. required). An additional 12.4 gms was added and then diluted to a net of 2000 gms. for a final pH of 2.6. After cooling to 30°C the gelatin solution was added to the collagen slurry with stirring over a fifteen minute period. Mixed twenty minutes longer and filtered through a stainless steel screen to remove any lumps. The filtrate was deaerated in a vacuum chamber at 30 inches of vacuum. The final slurry was then used to cast films of varying thickness on Mylar surfaces.

COLLAGEN - GELATIN FILMS 1 : 1

<u>FILM KNIFE SETTING</u>	<u>FILM THICKNESS Mils.</u>	<u>He TRANSMISSION cc/100in.²/24 hrs./atm.</u>	<u>TENSILE STRENGTH lbs./sq. in.</u>
0.025"		porous	-
.032"	-	porous	-
.040"	1.65	25.84	2710
.050"	2.4	26.24	2550
.060"	2.3	88.6	3512
0.075"	2.95	17.8	3142
0.100"	3.55	14.2	5120
0.150"	4.48	8.09	6060
0.200"	4.78	6.05	6690

A second set of films was prepared using an improved process for the preparation of the collagen in which we used 65% isopropyl alcohol to dewater the fibers. The mixing of the gelatin and collagen were performed more slowly resulting in better collagen dispersion in the mix. The amount of collagen was decreased to a collagen-gelatin ratio of 1 to 1.25.

100 gms of dewatered collagen fibers (containing 30% solids) and 900 gms of distilled water were slurried and cooled to 20°C. 41 gms of gelatin swelled in 1500 gms of water, melted, cooled to 35°C and added 7 gms of 85% lactic acid. Added 12.4 gms more of 85% lactic acid and diluted to 2000 gms. This gelatin solution was added dropwise to the collagen slurry using a dropping funnel over an hour's period of time. The addition was particularly slow at the beginning so that the paddle had a maximum opportunity to work the doughy collagen. This working resulted in a more effective dispersion of the collagen as the addition proceeded. The final mix was filtered through a stainless steel screen, deaerated in a vacuum chamber and cast into films using a #361 Gardner knife.

COLLAGEN - GELATIN FILMS 1 to 1.25

<u>KNIFE SETTING</u>	<u>FILM THICKNESS IN Mils.</u>	<u>He TRANSMISSION cc/100in.2/24 hrs./atm.</u>	<u>TENSILE STRENGTH lbs./sq. in.</u>
0.050"	1.57	39.89	1735
0.060"		Porous	
0.070"		Porous	
0.080"	2.47	21.1	2724
0.090"	2.64	15.1	3937
0.100"	2.98	17.18	3380

Inspection of the data showed that the use of collagen appeared to impart no beneficial characteristics to a gelatin film. While the values are somewhat erratic, their average indicated no superior qualities either in helium impermeability or in tensile strength. Consequently, we have eliminated collagen fiber reinforced films from the program.

d. Cellulose Fibers.

The use of cellulose fibers appeared to offer the best chance of success. Dispersion of cellulose fibers in a gelatin solution prior to casting have usually resulted in an uneven distribution of the fibers in the film. A more workable approach has been the use of a preformed layer of fibers and applying this to the gelatin solution to yield a film containing cellulose reenforcing fibers. The material best suited for this application has been lens paper. It is very thin, has long fibers and is free of fillers. This paper has a definite fiber direction, but this appeared to have little effect upon the film properties. It was easier to keep flat if the paper direction was maintained perpendicular to the long direction of the film. Also, a slight

tension on the paper while in the gelatin solution yielded better specimens. A pull of not more than 33 grams per centimeter of paper edge seemed to be adequate. Thus our films of 15 cm. width were subjected to a 500 gm. pull uniformly distributed along the edge. It was discovered early that if dry portions of the cellulose sheet projected beyond the gelatin solution, there would be wrinkles due to the stretching of the wet sheet. The best results were obtained when the cellulose sheet was cut smaller than the gelatin film. However, in order to permit handling, the sheet was made larger than the film in the long direction. Applied to an actual example this meant that for a gelatin film 55 x 15 cm the cellulose sheet was 65 cm x 14 cm and was laid into the fluid gelatin. The cellulose sheets were cut with, across and on a bias with the direction of the cellulose fibers. The least amount of wrinkling occurred when the fibers were perpendicular to the long dimension of the film. Almost as good results were obtained with the fibers on a bias.

Evaluation of the films disclosed that only one of the three films had the necessary impermeability, namely the film in which the cellulose fiber direction was perpendicular to the film length. Since the permeability is not likely to be directly related to the fiber direction, we must conclude that the incidence of successful film preparation with cellulose reenforcing fibers is low. The film itself was good having a helium transmission of 6.56 cc/100in.²/24 hrs/atmosphere and the tensile strength was 8370 lbs/in.². These values compare favorably with the best values obtained using gelatin alone but because of the difficulties encountered during the preparations we elected to eliminate the cellulose fiber reenforced films from further consideration until a definite need for them is indicated.

ORIENTATION OF FILMS

Attempts were made at orientating the molecules in a gelatin film by heating three mil films containing five percent glycerol under tension. The specimens, 40 x 15 cm were stretched between two 500 gram loads and heated by infra-red lamps to 167-170°C. The films shrunk rather than stretched, the amount of shrink being about 0.5% or 2 to 3 mm for the specimens being used. The lack of stretching probably meant that no appreciable amount of orientation had taken place. This idea will be further evaluated using the behavior of the film on the torsion pendulum as a criterion of its utility.

FINAL SELECTION OF FILM FORMULATION

The film composition chosen as possessing the optimum properties had the following composition:

Gelatin 100 parts

Glycerol 16 parts

Ox Bile 1 part

A stock pile of twenty-four films, 55 x 30 cm was prepared using the above formula with the necessary amount of water.

Samples of these films after the usual conditioning treatment at 73°F and 50% relative humidity for a minimum of twenty-four hours, were evaluated for gas transmission and tensile strength with the following results:

UNTREATED

CONTROL

GAS TRANSMISSION

Hydrogen	12.15	cc/100sq.in./24 hrs./atm.	
Helium	23.08	" "	" "
Oxygen	0.302	" "	" "
Nitrogen	0.0258	" "	" "
Carbon Dioxide	2.6	" "	" "

TENSILE STRENGTH

5040 pounds/ sq. in.

HEAT TREATED

Four samples of the film described above were heat treated in a forced draft oven at 101 ± 1°C for six days.

On evaluation for gas transmission and tensile strength the following results were obtained:

GAS TRANSMISSION

Hydrogen	4.66	cc/100sq.in./24 hrs./atm.	
Helium	9.97	" "	" "
Oxygen	0.0958	" "	" "
Nitrogen	0.053	" "	" "
Carbon Dioxide	0.616	" "	" "

TENSILE STRENGTH

4705 pounds/ sq. in.

ULTRA-VIOLET IRRADIATION

Two 55 x 30 cm films were exposed to two 100 watt mercury vapor lamps for a total time of thirteen days. After the irradiation, the films were conditioned at 50% relative humidity at 73°F. and evaluated for gas transmission and tensile strength.

GAS TRANSMISSION

Hydrogen	6.15	cc/100 sq.in/24 hrs./atm.		
Helium	16.62	cc	"	"
Oxygen	0.172		"	"
Nitrogen	0.032		"	"
Carbon Dioxide	1.57		"	"

TENSILE STRENGTH

3,790 lbs./sq. in.

The twelve samples of gelatin film were subjected to a -195.6°C. treatment with liquid nitrogen for two to three hours. After conditioning at 50% relative humidity and 73°F. for twenty four hours, the samples were evaluated with the following results:

GAS TRANSMISSION

Hydrogen	9.77	cc/100 sq.in./24 hrs./atm.		
Helium	21.54		"	"
Oxygen	0.466		"	"
Nitrogen	0.051		"	"
Carbon Dioxide	5.52		"	"

TENSILE STRENGTH

3,620 lbs./sq.in.

TORSION PENDULUM STUDIES

At the request of the project monitor Mr. David Lawson, we originally planned to build a torsion pendulum as described by Koppelman, Von Jan, Kolloid Z. 144, 22 (1955). The device was to be used for the study of the reported brittleness of gelatin films after exposure to cryogenic temperatures.

The availability of commercial torsion pendulums persuaded us to consider one of these rather than undertake the construction ourselves. As the result of a trip to Jet Propulsion Laboratory, Dr. T. H. Donnelly of Swift selected as the appropriate instrument and the corresponding auxiliary apparatus the following:

- 1 - Direct Recording Torsional Pendulum Item No. 100,628 Master Test Unit including Test Stand, Transducer, Inertia Discs, Environmental Housing 345,000 from Plas-Tech. Equipment Corp. of Natick, Mass. also,
- 1 - #500 - 603-000-1866-6-002-001-145-146 Speedomax Type W Recorder.
- 12 - #491,866 Speedomax W Strip Chart Paper - 200°C to +150°C.
- 1 - No. 8784-T-3-3-18-A Copper-Constantin Swaged Thermocouple 18" long from:

Leeds & Northrup Co., of
Park Ridge, Illinois

In addition we have received from Jet Propulsion Laboratory the following government property on a loan basis:

- | | |
|---------------------------|-------------------|
| 1. Oscilloscope Tektronic | 532 J-270-F-47436 |
| 2. Type H Plug-in | LA-61817 |
| 3. H. P Oscillator | J-270F-2883 |
| 4. Voltmeter H H.P. 400D | J-270F-8243 |
| 5. Camera C-12 | J-270F-14369 |

Mr. D. Lawson has set up the equipment for us and has checked it out against actual gelatin samples. The new contract continuation has now been received and subsequent work will get under way as of August first to carry out the program.

A limited amount of experimental work has been carried out in the preparation of massive specimens of gelatin. The best results were obtained from gelatin solutions containing about 25% solids poured onto glass. These could then be cut with scissors before complete drying or by scoring and snapping after complete drying. Sufficient samples are available to permit us to familiarize ourselves with the workings of the instrument.

FUTURE WORK

Initially we will follow the plan of approach outlined in the modification I of Contract NAS 7-487. The plan given there will enable us to orientate ourselves as to results to be expected and the direction which subsequent work should take.

FINANCIAL

The number of man hours used in this fiscal period is 152 amounting to an expenditure of \$1,795.12. The total hours and expenditures expended in the contract to date is 1943 hours and \$22,977.14 or 99.47% of the total. Any unused balance will be carried over into the second twelve months of the modified contract.

HARLAND H. YOUNG

HHY:LL